Literature Review of the Health Effects Associated with the Inhalation of Hydrogen Sulfide

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INTRODUCTION

This document summaries information about the health effects associated with inhaling hydrogen sulfide. It presents a review of occupational and environmental epidemiological studies and animal studies on low-level exposures to hydrogen sulfide. Hydrogen sulfide is also of concern because it can damage property and create objectionable odors. Exposure to objectionable odor may be considered a health hazard because odor may adversely affect the well-being and mental health of impacted people. In addition, the corrosive effects of hydrogen sulfide may damage metals and other property at low levels.

Potential Sources of Hydrogen Sulfide

Hydrogen sulfide is a colorless, flammable gas that is heavier than air. It is also called hydrosulfuric acid, stink damp and sewer gas. Hydrogen sulfide occurs naturally and can be found in volcanic gases, petroleum deposits, natural gas, and hot springs (ATSDR 1999). Hydrogen sulfide is formed when organic matter undergoes putrefaction. Hydrogen sulfide can be found in sewage treatment facilities, fish aquaculture and in areas where livestock or manure is handled (ATSDR 1999). Much of the public concern about confined animal feeding operations has centered on hydrogen sulfide emissions. Hydrogen sulfide is also present in emissions from industrial paper plants that use the Kraft Process. The leather industry uses hydrogen sulfide to remove hair from hides before tanning and tons of hydrogen sulfide have been used by facilities for the production of heavy water for nuclear reactors (Klaassen et al. 1996). Industrial sources of hydrogen sulfide also include petroleum refineries, natural gas plants, petrochemical plants, coke oven plants, and food processing plants (ATSDR 1999).

Ambient Concentrations

Average background concentrations in the air in the US are estimated to be between 0.11 and 0.33 ppb (0.15 and 0.46 $\mu g/m^3$). In undeveloped areas of the U.S., concentrations have been reported to range between 0.02 and 0.07 ppb (0.028 and 0.09 $\mu g/m^3$)(ATSDR 1999).

Air concentrations can be expressed in units of milligram per cubic meter (mg/m^3), microgram per cubic meter ($\mu g/m^3$), parts per billion (ppb), or parts per million (ppm). One mg is 0.001 gram (g) or 10^{-3}g, 1 μg is 10^{-6} g (one millionth of a g) and there are 1000 μg in a mg. To convert units for hydrogen sulfide, $1.417 \times ppm = mg/m^3$ and $1.417 \times ppb = \mu g/m$.

Environmental Fate and Transport

Hydrogen sulfide released into the atmosphere is reactive and is estimated to remain for an average of about 18 hours. It may contribute to the formation of sulfur dioxide and sulfuric acid in the atmosphere, contributing to acid rain (ATSDR 1999).

Monitoring in Idaho

DEQ is in the process of developing a monitoring program to assess hydrogen sulfide emissions. Preliminary monitoring results indicate levels of hydrogen sulfide in the ambient air in some areas that might have potential adverse impacts on exposed populations.

HEALTH EFFECTS

Hydrogen Sulfide is very toxic. The health effects caused depend on the amount and duration of the exposure. The health effects most relevant to development of an ambient air standard are those caused by low-dose, long-term exposure to hydrogen sulfide through inhalation of the ambient air. Effects resulting from short term relatively high exposures are well documented and are of great concern for occupational safety and health. Exposure to lower concentrations of hydrogen sulfide can cause eye irritation, respiratory tract irritation and symptoms like a sore throat and cough, shortness of breath, accumulation of fluid in the lungs and memory changes.

There are many studies of workers and others exposed to high and moderate doses of hydrogen sulfide. We focused our review on low-dose, longer-term exposures. Hydrogen sulfide does not accumulate in the body and is not a cumulative toxicant at low exposures.

Exposure to Lower Concentrations

Hydrogen sulfide is a potent eye and mucous membrane irritant at relatively low concentrations (50-200 ppm). Hydrogen sulfide is a respiratory tract irritant and exposures greater than 20 ppm can cause irritation of the mucous membranes. Respiratory and eye irritation at levels of 50-200 ppm are well documented. Levels of 50-100 ppm or 70-140 mg/m^3 cause respiratory tract irritation in healthy individuals (Berger 1996). Respiratory irritation may decrease the ability of people to fight off infection. Generally pulmonary function tests changes are not seen in healthy people exposed to 5-10 ppm. However, asthmatics have shown changes in pulmonary function following exposure to 2 ppm for 30 minutes (Jappinen et al 1990). Eye irritation is another sensitive effect. The Agency for Toxic Substances and Disease Registry (ATSDR) (1999) attributed to National Institute of Occupational Safety and Health (NIOSH) the statement that “ocular effects occur at concentrations that provide no other observable systemic effect”. Whether the eye or the respiratory tract is more sensitive to hydrogen sulfide probably varies greatly among different individuals. The US Environmental Protection Agency (EPA) chose “inflammation of the nasal mucosa” as the health effect of concern for their reference concentration (explained in more detail in the following section). Because data on neurological and immunological effects are lacking, respiratory irritation may be the most sensitive health endpoint for which there are good data.

Exposure to Very Low Concentrations

The effects of prolonged low-dose exposures have not been well studied. Long term exposure to low concentrations has been associated with neurological symptoms, including: fatigue, loss of appetite, irritability, impaired memory, altered mood states, headache and dizziness (ATSDR 1999; Kilburn and Warshaw 1995; Schiffman et al.1995; Beauchamp et al. 1984; Berger 1996). Effects of this type are difficult to measure and study.

Neurological damage after high dose exposures is well documented. Neurobehavioral disfunction and profile of mood states have been affected in workers and residents exposed to low levels of hydrogen sulfide, but many of the people examined were self-selected for the studies (Kilburn and Warshaw 1995; Schiffman et al.1995). The mechanism of neurological damage from low doses is not clear. It may be worth noting that asthmatics doing vigorous exercise (mouth breathing) did not complain of headache and nausea but experienced respiratory effects (Tatum 1998).

Effects like headache, nausea, appetite loss, irritability and fatigue may occur with perception of unpleasant odor. Both Thu (1998) and Schiffman (1995; 1998) have studied odor-related health effects. The reported odor threshold for hydrogen sulfide varies greatly but is generally reported to be less than 10 ppb. Some people may be able to detect the odor of hydrogen sulfide in air at concentrations as low as 0.5 ppb (ATSDR 1999). Odor from hydrogen sulfide can be annoying and affect well-being. Whether or not unpleasant odors should be viewed as a nuisance or as something that causes emotional stress and might constitute a public health issue is debated. Certainly, effects on well-being may affect immunity and susceptibility to disease (Weisse 1992) therefore headache and nausea should be considered health effects.

Sensitive People

Whether children are more sensitive to the effects of hydrogen sulfide than adults and whether exposure to hydrogen sulfide can cause birth defects is not known (ATSDR 1999). Often the neurological systems of developing fetus, infants and children are more sensitive to neurotoxins than adults, but there is little information available on differences in sensitivity for hydrogen sulfide.

Because of the odor and irritancy effects of hydrogen sulfide, asthmatics would be expected to be more sensitive than the general population.

Case Studies and Clinical Studies

Respiratory and Eye Effects

Jappinen et al. 1990 studied 26 Finnish pulp mill workers exposed to levels of hydrogen sulfide less than 10 ppm and 10 asthmatics exposed to 2 ppm hydrogen sulfide in a laboratory situation.

They found that two of the asthmatics experienced bronchial obstruction after exposure to 2 ppm for 30 minutes, but no statistically significant changes were seen in the group overall. An exposure to 10 ppm for 4-7 hrs resulted in conjunctivitis and 1 hour of exposure to about 50 ppm caused eye and, respiratory tract irritation.

In 1982, Bhambhani et al. initiated a series of controlled studies of healthy exercising men and women, after concern about an oil well blowout in Alberta. In a 1991 study, men were exposed to 0, 0.5, 2.0 and 5.0 ppm hydrogen sulfide while cycling. Blood lactate levels and oxygen intake were increased at 5 ppm. It is thought that blood lactate levels are an indicator of cytochrome oxidase inhibition, which may be related to neurological effects seen at low-level exposures. The No Observable Adverse Effect Level (NOAEL) for the study was about 2.0 ppm and the Lowest Observable Adverse Effect Level (LOAEL) was 5.0 ppm. A study published by the same group in 1994 demonstrated no adverse health effects in healthy men and women exposed to 5.0 ppm for 30 minutes. Respiratory effects and blood lactate levels were not affected. In 1996, Bhambhani et al. found a NOAEL for respiratory effects of 10.0 ppm (Bhambhani et al. 1996).

Neurological Effects

Jappinen et al (1990) published reports of headache in three of ten asthmatics exposed to 2 ppm hydrogen sulfide for 30 minutes. No statistically significant changes in pulmonary function of workers or asthmatics were detected but three of the ten asthmatics reported headaches.

A 20 month old infant exposed to hydrogen sulfide (levels up to 0.6 ppm for about 1 year) and other emissions from a coal mine exhibited ataxia, distonia, and other effects on the central nervous system. The child was diagnosed with toxic encephalopathy with neurological symptoms. The symptoms reversed ten weeks after the infant was removed from exposure

(ATSDR 1999; Kaderly 1997). The contribution of hydrogen sulfide versus other contaminants in air from the mine is unclear.

Occupational Exposures and Epidemiological Studies

Workers in industries such as pulp and paper mills, makers of rayon textiles, petroleum and natural gas drilling operations and wastewater treatment plants, manure pits and landfills may be exposed to higher levels of hydrogen sulfide than the general population (ATSDR 1999).

Respiratory and Eye Effects

Inflammation of the cornea of the eye has been reported in workers exposed to 10 ppm hydrogen sulfide for 6 hours (EPA 2000).

Donham et al. (1995) studied workers in a yard where swine were confined. Workers were evaluated for respiratory diseases and significantly more swine workers than control workers reported bronchitis, but this may have due to exposure to ammonia, dust and endotoxins rather than hydrogen sulfide.

Neurological Effects

Neurological effects in workers after acute exposure are well documented. Researchers have observed fatigue, memory loss, dizziness and irritability increases in workers after chronic exposure (Beauchamp et al. 1984). Studies done in the late 1980s found a lack of mental concentration, chronic headaches, and a variety of central nervous system symptoms in workers in the pulp industry. Chronic exposure in shale workers has been associated with complaints of headache, loss of appetite, fatigue, irritability, poor memory and dizziness (Kaderly 1997).

Community Exposures and Epidemiological Studies

Some environmental epidemiology studies have found associations between symptoms and low level exposure and others have not.

Respiratory Effects

In 1998, Bates et al. conducted a retrospective epidemiological study using hospital discharge data from Rotorua, New Zealand where geothermal energy is used and median hydrogen sulfide concentrations are estimated to be about 20 $\mu g/m^3$ (14 ppb) with 35 % of the measurements less than 70 $\mu g/m^3$ (49 ppb) and 10% greater than 400 $\mu g/m^3$ (280 ppb). Bates et al. (1998) discovered significant increases in nervous system and sensory diseases in Rotorua residents.

A series of papers have been published on associations found as a part of the South Karelia Air Pollution studies which was initiated in 1986 to assess the symptoms of residents living near paper and pulp mills in Finland. The study focused on three communities; one with severe air pollution, one with moderate air pollution and a control, relatively unpolluted community. Most of the publications reported concentrations of total reduced sulfur (TRS) compounds, about 2/3rds of which was thought to be hydrogen sulfide. Although mean concentrations in polluted communities where people reported symptoms of cough and headache were as low as 1-2 $\mu g/m^3$, the daily average concentrations were as high 56 $\mu g/m^3$ (40 ppb)(ATSDR 1999). Jaakkola et al. (1990) reported significant differences in respiratory symptoms in the three towns; one severely

(44 μg/m^3, 2.9 ppb mean, 56 μg/m^3, 40 ppb maximum;), another moderately (2 μg/m^3, 1.4 ppb mean and 22 μg/m^3, 16 ppb maximum) and the third, not polluted by pulp mill emissions. Self-administered questionnaires were used to assess symptoms. The occurrence of cough and eye and nose irritation were statistically greater in the more exposed communities (Jaakkola 1990). Marttila et al. (1994) found nasal symptoms and cough were increased one year and several years later and their evaluation showed an exposure-related increase in nasal symptoms and pharyngeal irritation (Marttila et al. 1994). Eye, nose irritation, cough, headache, among exposed children were greater than the children in the unpolluted community (Marttila 1994). Jaakkola et al (1990) also reported that infant and preschool children in the polluted city with ambient concentrations averaging about 1 ppb, had a higher rate of respiratory infection than the reference city population. The results of this research study suggested that eye and nasal irritation and cough occurred more often among those exposed to levels of TRS ranging up to 70 ppb (daily average) and annual mean concentrations of 6 ppb, than unexposed people. The researchers observed "slightly more" chronic bronchitis and asthma in the more severely polluted communities. The authors concluded that the WHO standard of 0.1 ppm, (24 hour) does not protect against eye, nose symptoms and cough. (Jaakkola et al. 1990). People living in the communities near the pulp and paper mills, recording mean annual concentrations of 6 μg/m^3 or 4.3 ppb with daily peaks as high as 100 μg/m^3 or 70 ppb, reported 12 times more eye irritation than those in the reference community (Jaakkola et al. 1990). These studies were focused on the industrial town of Imatra, where both adults and children living near a pulp mill reported "an excess of persistent eye symptoms, respiratory symptoms and headache and migraine" compared with people who lived in a nonpolluted reference community. In the later publications, the most polluted study area had annual mean concentrations of 8 μg/m^3 hydrogen sulfide. The highest concentration measured in a 24 hour period was 100 μg/m^3. In a study where daily reporting of symptoms and daily monitoring was done, more headache, depression, tiredness and nausea were reported when TRS concentrations exceeded 40 μg/m^3.

Partti-Pellinen et al. (1996) followed up with an assessment of symptoms associated with lower concentrations in another community in Finland, Varkaus, where a more modern process was used and emissions were lower. These researchers assessed respiratory as well as eye and nervous system effects in a polluted community (2-3 μg/m^3 mean, 155 μg/m^3 maximum) and the reference community. They found more eye and nasal irritation, cough, increased reporting of acute respiratory infections. The researchers concluded that in an exposed community with annual mean concentrations of total reduced sulfur compounds of 2-3 μg/m^3 residents reported an excess of cough, respiratory infections and headache (Partti-Pellinen et al. 1996)

Dales et al. (1989) found that emissions from oil refineries in Canada led downwind residents to report respiratory symptoms and produced impaired pulmonary function in the residents.

Berger (1996) did a masters thesis study designed to determine if airborne hydrogen sulfide from a landfill was related to self-reported signs and symptoms among self-selected, local residents. Residents lived in an area adjacent to and lower than the landfill. Levels as high as 782 ppm were detected above the landfill. Air escaping the landfill in pockets had levels from 20-128 ppm and levels greater than 100 ppm were consistently found. Headache and eye irritation were the most commonly reported symptoms. Respiratory infection, nasal and throat irritation were also reported.

In a case-control study of residents in Puna, Hawaii, researchers assessed exposures from geothermal wells. They found no association between respiratory conditions and exposure to air concentrations, which ranged from 5-11 ppb (Brooks et al. 1993).

Several studies have linked asthma to exposure to air pollution, which may have included hydrogen sulfide. Most of these studies have involved distributing questionnaires to parents of children living near a pulp plant, refinery or another source of pollution and generally levels have not been monitored. Toxic chemicals and many types of smoke and particulates, including second hand cigarette smoke, may increase the occurrence of allergic asthma. Studies like these, involving exposures to a mixture of pollutants, are difficult to use for establishing ambient standards.

Neurological Effects

The South Karelia Air Pollution Study of communities near pulp mills in Finland found that exposure to hydrogen sulfide caused people to report more headaches, depression, tiredness and nausea. These symptoms were reported on days when the 1 hour or daily averages exceeded 0.028 ppm or 40 $\mu g/m^3$. The relative risk for headache was estimated to be significantly greater in the exposed community. Concentrations of sulfur dioxide were said to be similar in both communities (Partti-Pellinen et al. 1996).

In their study of New Zealand hospital discharge data described above, Bates et al. (1998) found statistically significant increases in central and peripheral nervous system disorders including migraine headache, and infant cerebral palsy.

Neurobehavioral functions and profile of mood states were measured in 13 former workers and 322 neighbors of a crude oil refinery that had complained of headache, nausea, vomiting, personality changes, nosebleeds and breathing difficulties. A plaintiff's law firm helped support the study. Hydrogen Sulfide emissions were estimated to average from 0 – 8 ppm daily and TRS exposures near the plant were estimated to be 1 – 71 ppm. Measured concentrations at the street near subjects home during 1 week averaged 10 ppb with periodic peaks of 100 ppb. The group was matched for age and educational level to a control group. Reaction time, balance, color discrimination, digit symbol, trail-making and immediate recall of the exposed subjects were abnormal and the profile of mood states scores were high in both workers and residents, compared to controls. The authors concluded that neurophysiological abnormalities were associated with exposure to reduced sulfur gases, including hydrogen sulfide from crude oil desulfurization (Kilburn and Warshaw 1995). Their study suggested long term, continual, low exposure in residents might produce more effects than higher, 40 hour/week, for 3-4 year exposures in workers. Dose response relationships were not established.

Schiffman et al. (1995) evaluated 'profile of mood states', using two measures, for 44 residents near a large scale swine operation and compared them to a control population. Levels of emissions were not measured. The experimental group reported significantly more tension, depression, fatigue, anger, confusion and less vigor than the control group. Residents were exposed to a mixture of odoriferous compounds including hydrogen sulfide, mercaptans, aldehydes and volatile organic acids.

Exposures from hydrogen sulfide emitted from an industrial waste lagoon in Terre Haute, Indiana resulted in people being exposed to air concentrations estimated to be about 0.3 ppm. Health complaints reported included: nausea, sleep loss, headaches and shortness of breath (Indiana Air Pollution Control Board 1964).

Headache was a commonly reported symptom in residents adjacent to a Florida landfill emitting hydrogen sulfide (Berger 1996).

Studies on Laboratory Animals

Many animal studies have been conducted and summaries and abstracts of many were reviewed for this assessment but very few involve low-dose, long term exposure. Results of human studies, especially the community epidemiological studies, are much more applicable to standard development than the animal studies that have been conducted.

The EPA used the results of a subchronic (90-day) inhalation study of mice conducted in 1983 to develop an RfC. A 1983 study done at the Chemical Industries Institute of Toxicology

(CIIT) on two strains of rats found a NOEAL for respiratory tract inflammation of 30.5 ppm (CIIT 1983). ATSDR also used this NOAEL to derived an Minimal Risk Level (MRL) of 0.3 ppm using an adjustment for extrapolating from rats to humans, and an uncertainty factor of 30 (ATSDR 1999)

Developmental effects in animals have not been well demonstrated. Levels of 20-75 ppm were reported to cause neurological changes in developing nervous system in a study of prenatal development in rats. ATSDR summarized a study by Hannah and Roth (1991) in which pregnant dams and their pups were exposed from 5 days postcoital to 21 days postnatal to 20 ppm or 50 ppm for 7 h/d. They noted severe alterations in architecture and growth patterns of Purkinje cell dendritic fields at both doses. The authors concluded “low concentrations of hydrogen sulfide place developing neurons… at risk of severe deficits”.

Established EPA and ATSDR Chronic Threshold Values used for Superfund Risk Assessments

ATSDR established an MRL, which they define as an estimate of human daily exposure to a substance that is likely to be without appreciable risk of adverse noncarcinogenic effects over a specific duration of exposure. The MRL most relevant to development of an ambient air standard would be a chronic duration inhalation MRL that ATSDR has not yet been developed due to insufficient data. ATSDR has developed an MRL of 0.03 ppm for intermediate-duration inhalation based on the NOAEL for respiratory effects in mice and an MRL of 0.07 ppm for acute-duration inhalation based on respiratory effects in people with asthma. Based on the a LOAEL of 2 ppm for the respiratory effects of bronchial obstruction in asthmatics reported by Jappinen et al. (1990), ATSDR derived an MRL of 0.07 ppm using an uncertainty factor of 30. These MRLs may not be protective for health effects that may be acquired following repeated acute insults, such as hypersensitivity reactions, asthma or chronic bronchitis. A chronic-duration MRL was not developed by ATSDR “since data were insufficient” (ATSDR 1999).

The EPA Reference Concentration (RfC), published On-Line in the Integrated Risk Information System (IRIS) database, is defined as “an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily inhalation exposure of the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime.” The RfC for hydrogen sulfide was developed from the NOAEL (30.5 ppm or 1.01 mg/m^3) and a LOAEL (80 ppm or 2.6 mg/m^3) for inflammation of the nasal mucosa and from the results of a subchronic (90-day) inhalation study of mice conducted by CIIT in 1983. The EPA applied an uncertainty Factor of 1000, using a factor of 10 to protect sensitive individuals, a factor of 10 to adjust from subchronic studies to a chronic study, and a factor of 10 for both interspecies conversion and database deficiencies. The resulting RfC was 0.001 mg/m^3, which can also be expressed as 1 $\mu g/m^3$, 1×10^{-3} mg/m^3 or 0.7 ppb (EPA 2000).

In 1995, when the information on inhalation toxicity in IRIS was last updated, the EPA determined that the human occupational and case study literature was not an adequate basis for an RfC because exposure levels were generally poorly defined and results were confounded by concurrent exposure to other toxicants. They also noted that community epidemiological studies have also failed to define exposures (EPA 2000).

The State of California derived a chronic reference exposure level (REL) of 200 $\mu g/m^3$. (140 ppb). The REL is defined as a concentration below which adverse health effects are not likely to occur. A chronic REL of 10 $\mu g/m^3$, or 8 ppb resulted when respiratory effects in animals were used as an endpoint, and multiple safety and uncertainty factors were applied (California EPA 2000). The ambient air standard for California, based on a one hour averaging time is 42 $\mu g/m^3$ or 30 ppb.

Table 1.0 Summary of Threshold Values developed by applying safety factors, uncertainty factors and/or modifying factors to No Observable Adverse Effect Levels found in human and animal studies.

Threshold Value	Duration of Exposure	Value	Health effect endpoint
MRL	Intermediate	0.03 ppm, 30 ppb (42 μg/m^3)	respiratory effects in mice
MRL	Acute	0.07 ppm, 70 ppb (98 μg/m^3)	respiratory effects in people with asthma
RfC	Subchronic	0.0007 ppm, 0.7 ppb (1 μg/m^3)	inflammation of the nasal mucosa.
REL	Chronic	0.008 ppm, 8 ppb (10 μg/m^3)	Respiratory effects in animals

Corrosion of Materials and Effects on Vegetation and Animal life

Hydrogen sulfide in air may attack and corrode copper, silver, zinc, lead, aluminum, iron and other metals. The corrosive effect, evident as rust or tarnish, has been demonstrated on metals exposed to levels of 0.01 ppm for 30 days. Copper may be the most sensitive metal and copper components are important for outdoor electrical equipment. Corrosion of copper is of concern because of the importance of electronic equipment reliability. Increased moisture in the air increases corrosion. Some states have proposed lower standards for areas with higher relative humidities. For example, Nebraska proposed a standard of 0.01 ppm 30-day for relative humidity < 60% and 0.005 ppm when relative humidity is > 60 % based on welfare effects (preventing corrosion to structures). These standards are lower than Nebraska's health-based standard of 0.1 ppm for 30 minutes. The State of Pennsylvania based their welfare standard of 0.005 ppm on the effect of darkening exterior lead based paint (Kaderly 1997).

Although hydrogen sulfide has adverse effects on crops and vegetation, corrosion effects occur at lower levels than those damaging vegetation so standards set to protect from corrosion protect vegetation as well.

State Standards, Guidelines

State standards have been derived for heath effects, odor, or nuisance or welfare effects.

Table 2.0 Summary of State Ambient Air Guidelines, Standards, Advisories and Recommended Exposure Limits. Many of these standards were developed in the 1970s before results of many of studies about neurological and respiratory effects were available.

State	Concentration in ppm	Concentration in μg/m^3 [b]	Averaging Time
Alabama	20		30 minutes
Alaska	0.035		30 minutes
Arizona	0.08		1 hr , welfare[a]
	0.13		1 hr , welfare
California	0.03	42	1 hr, welfare, nuisance
Colorado		1.42	1 hr welfare
Delaware		0.06	3 minutes, health and nuisance

	0.03		1 hr
Hawaii	0.025		1 hr, welfare
Illinois	0.01		8 hrs, health-based
Kentucky		14	1 hr
Louisiana		33	8 hr
Maryland		3.79	24 hr
Massachusetts		3.79	24 hr
		3.79	annual average
Michigan	0.0007[c]		24 hr
	0.0045		10 minutes, nuisance
Minnesota	0.05	70	Averaged over 30 minutes and not to be exceeded more than 2 times/yr
	0.03	42	Averaged over 30 minutes and not to be exceeded more than 2 times in any 5 consecutive days.
Missouri	0.05	70	Averaged over 30 minutes and not to be exceeded more than 2 times/yr
	0.03	42	Averaged over 30 minutes and not to be exceeded more than 2 times in any 5 consecutive days.
Montana	0.05	70	1 hr
Nebraska	0.1		30 minutes
	0.01		30 day average, welfare
	0.005		30 day average, welfare
Nevada	0.08		1 hr
New Hampshire	0.03		24 hr
		467	Ceiling
New Mexico	0.1		1 hr
New York	0.01		1 hr
	0.0007		Annual
North Carolina	1.5		15 minutes
North Dakota	0.2	280	1 hr, Not to exceed once/month
	0.1	142	24 hr, Not to exceed once/yr
	0.02		90 day, welfare
Oklahoma	0.1[e]		30 minutes
Pennsylvania	0.005		24 hr, welfare
Rhode Island		142	Ceiling
South Carolina	0.1	142	24 hr
Tennessee	20		12 hour
Texas	0.08		Health and welfare
		0.9	24 hr
Vermont	0.02	33.3	24 hr
Washington		0.9	
Wyoming	0.02		24 hr
	0.05	70	30 minutes, not to exceed twice/yr
	0.03	40	30 minutes, not to exceed twice in 5 consecutive days

a A welfare standard or guideline is developed for nuisance effects, crop damage or other effects rather than health effects in people

b Many of these values were compiled by ATSDR in their Toxicological Profile (1999). Supporting documentation for many was not available. Individual states were not contacted to verify the accuracy of the values reported by ATSDR.

c Reported by (Kaderly 1997) as a standard adopted in 1992.

d Reported in Filer Township Human Health and Safety Committee (1997).

e ATSDR (1999) reported a 3 minute standard of 0.1 ppm for Oklahoma.

Occupational Standards

Occupational standards have been established for short-term high level exposures to hydrogen sulfide. OSHA has established an acceptable ceiling concentration of 20 ppm for hydrogen sulfide in the workplace with a maximum level of 50 ppm allowed for a maximum of 10 minutes time. OSHA's Permissible Exposure Limit (PEL) is 10 ppm averaged over an 8 hour work shift. OSHA's Short Term Exposure Limit (STEL) is 15 ppm for any 15 minute period (ATSDR 1999). NIOSH has set a recommended exposure limit ceiling value of 10 ppm, 15 mg/m^3 for 10 minutes exposure (NIOSH 1994).

The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value, time weighted average is 10 ppm.

CONCLUSIONS

The critical effects or effects that occur at the lowest concentration of hydrogen sulfide and affect the most sensitive system in the body are probably neurological effects. What exposure concentrations can cause these effects in sensitive people is unclear. Neurological effects, especially neurological effects on the developing fetus, have not been studied adequately at low exposure concentrations and there is a lack of information from which to derive threshold levels for sensitive neurological endpoints. Respiratory effects and eye irritation are better demonstrated but appear to occur at higher concentrations than effects like headache and fatigue. Inflammation of the nasal mucosa was judged by the EPA to be the best effect for assessing health risk from inhalation of hydrogen sulfide.

Case studies and epidemiological studies must be interpreted carefully due to many confounding factors, biases, and multiple exposures. It should be recognized that people in epidemiological studies were exposed to a mixture of toxicants. Animal studies are conducted under controlled conditions but extrapolating health effects observed in animals to health effects expected in humans is uncertain. Health-based air standards or values like the EPA's RfC are generally derived by applying safety factors and uncertainty factors to a NOAEL or to a LOAEL. Factors of 10 for extrapolating from mice to humans, another factor of 10 for extrapolating from subchronic exposure and another factor of 10 for protection of sensitive people or to account for the variability in sensitivity in a population are applied. The following is a brief summary of threshold type values reported in the literature.

• A LOAEL of 2 ppm was reported by Jappinen et al. (1990) for respiratory effects. A standard derived from Jappinen et al.'s (1990) study of adult asthmatics using a factor of 10 to help account for sensitive individuals and a factor of 10 for using a LOAEL rather than a NOAEL, might be as high as 0.02 ppm or 20 ppb. This might not protect child asthmatics that might be more sensitive than adults and would not be protective for neurological effects.

•To protect from respiratory effects the EPA derived an RfC, used for assessing risk from superfund sites, of 0.001 mg/m^3 (0.0007 ppm) or 1 $\mu g/m^3$ (0.7 ppb) (IRIS 2000).

•Data collected from the South Karelia Air Pollution Study suggests exposure to average concentrations as low as 1 – 8 $\mu g/m^3$ or about 1- 6 ppb might be associated with symptoms of headache, cough and increased respiratory infections in children. It is not clear how peak concentrations, which ranged more than ten times the average concentrations, may have influenced the symptoms. The residents studied were also exposed to a mixture of compounds, not just hydrogen sulfide.

• Studies by Bhambhani et al. (1996) suggest a NOAEL of about 2.0 ppm for a 30-minute exposure for blood lactate levels indicative of enzyme inhibition.

Odor

Some people may be able to detect the odor of hydrogen sulfide in air at concentrations as low as 0.5 ppb (ATSDR 1999). Exposure to objectionable odor may cause headache, nausea, appetite loss, irritability and fatigue may occur with perception of odor (Thu 1998; Schiffman 1995; 1998).

California EPA based it's standard on a mean olfactory perception level (average odor detection level) of 0.03 ppm or 42 $\mu g/m^3$. The standard was designed to protect against symptoms of headache and nausea due to odor. The agency has since proposed a lower standard, to protect from odor, of 10 $\mu g/m^3$. For the State of California, Amoore (1985) reviewed the literature and determined a log normal distribution for reported odor thresholds with a geometric mean of 10 $\mu g/m^3$, 8 ppb with a standard deviation of 4.

Defining annoyance in terms of behavior responses, nausea and headache, Amoore (1985) predicted that 50 % of the population would detect hydrogen sulfide at a concentration of 10 $\mu g/m^3$ under laboratory conditions, and about 5% would find this concentration annoying. Although Minnesota acknowledges that odor perception is not generally used as an adverse health effect on which to base inhalation standards, they also adopted a standard of 42 $\mu g/m^3$ (California EPA 2000; Minnesota Department of Health 2000).

Toxicological research suggests that the concentration of hydrogen sulfide needed to cause an adverse response in the respiratory system is higher than the concentrations at which the odor can be detected and odor responses are apparent. An exposure guideline to protect against headache, nausea and other effects that might be related to odor would be lower than a guideline based on respiratory effects.

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